Crystal growth and annealing study of the high-temperature superconductor $HgBa_2CuO_{4+\delta}$

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The flux crystal-growth method is used to grow reasonably sized, single crystals of the cuprate superconductor $HgBa_2CuO_{4+\delta}$ (Hg1201). One as-grown sample measured had a T_c of about 80 K with a sharp transition (~ 2 K), although signatures of non-uniform doping were observed. Another sample, which was annealed at 300°C at 8 bar of O_2 pressure, was successfully overdoped and had a T_c of about 84.5 K, with a transition width of about 2.5 K. This sample also proved to homogenous, with oxygen dopant being evenly distributed. Samples were therefore successfully grown and prepared for future measurements.

Introduction

Since 1911, superconductivity has been a well-observed and well-documented phenomenon [1]. It is characterized by a sudden drop to zero resistance when a metal is cooled below a certain critical temperature, denoted as the T_c. It is also characterized by another fundamental property known as the Meissner-Ochsenfeld effect. This property is the expulsion of all magnetic fields from the interior of the superconductor for sufficiently small fields [2]. Traditional superconductivity can be explain by BCS theory, which describes how electron-phonon interactions within the material are responsible for bringing the electrons all to the lowest possible energy state when cooled below the critical temperature. Applications of superconductors range from MRI machines to SQUID magnetometry. However, all these applications require that the superconducting material is cooled below its critical temperature, which is typically below 30 K for conventional superconductors. This changed in 1986, when superconductivity was discovered in a ceramic cuprate material with a T_c of about 30 K [4]. This was not only noteworthy due to the high T_c, but also because of the very different material that

superconductivity was found in (all superconductors up until that point had been metals). Since then, many other cuprates with even higher critical temperatures (up to about 164 K) have been discovered. These materials are known as high-temperature superconductors.

Superconductivity in the cuprates is believed to originate in the copper-oxygen planes of these materials. It has been experimentally shown that electron-phonon interactions are too weak in these materials to be the mechanism for superconductivity [7]. Therefore, there must be another mechanism involved. It is known that these materials do not display superconductivity without a certain level of doping. Knowing that the superconductive state of a material also depends on the temperature, we can construct a temperature vs doping phase diagram for these materials. A generic phase diagram is shown in Figure 1 below.

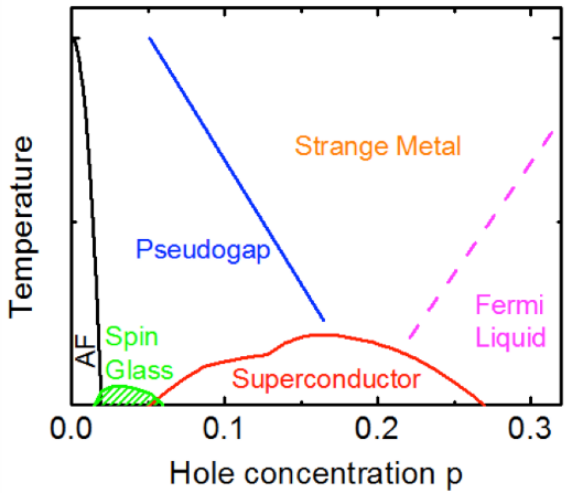

Figure 1: Generic temperature-doping phase diagram of the cuprates. The red line represents T_C.

It can be seen that the region where materials exhibit superconductivity forms a dome on the diagram. There are also other interesting phases displayed in this diagram. At sufficiently low doping levels, the materials are simply antiferromagnetic insulators. In the enigmatic pseudogap phase, there is a partial energy gap in the Fermi surface of the material and the resistivity was recently shown to be proportional to T^2, as is typically observed for conventional Fermi-liquid metals. In the strange-metal phase, resistivity is proportional to T, not T^2, which is a behavior that remains to be understood [2,3]. At very high doping levels, the cuprates have been known

for some time to behave like a conventional Fermi liquids. The reasons for all of these different regimes are still hotly debated. These and many other interesting properties are what make the cuprates desirable to study.

The material of interest in this study is $HgBa_2CuO_{4+\delta}$ (mercury barium copper oxide, also denoted as Hg1201). This is a very desirable material to study due to its symmetric tetragonal crystal structure and simple unit cell. This unit cell maintains its structure throughout a wide range of doping, and the CuO_2 planes are almost perfectly square, which may be linked to the higher T_c in Hg1201 [9]. This particular cuprate is also not as susceptible to disorder as the other cuprates. It is generally believed that disorder in a crystal system suppresses potential superconductivity. Disorder in Hg1201 stems primarily from Hg vacancies and interstitial oxygen dopants in the Hg layer. However, the Hg layers are relatively far from the CuO_2 planes, where superconductivity is believed to occur. Therefore, these causes for disorder have less effect on the CuO_2 planes [6]. The CuO_2 planes are also believed to have a simple square-lattice structure. The simplicity of this model cuprate will hopefully allow to better isolate the mechanism of high-temperature superconductivity.

For this reason, the aim of this study is to properly execute growths of single crystals of Hg1201, and successfully anneal a sample.

Crystal Growth and Preparation

The growth process of Hg1201 involves the synthesis of mercury, oxygen gas, barium oxide, and copper (II) oxide into the final product of mercury barium copper oxide. The complete chemical reaction is shown below:

$$2Hg+O_2 + 4BaO+2CuO \rightarrow 2HgBa_2CuO_4$$

In our lab, relatively large, single crystals are grown using the flux method for growing crystals [10]. This method involves a two-step process. In the first step, a mixture of $Ba(NO_3)_2$ and CuO is sintered at about 900°C with O_2 flow to form the precursor Ba_2CuO_3. The reason this sintering process is necessary is due to the unstable nature of the reactant BaO, which readily absorbs water and reacts with CO_2 in the air. Minimizing this effect allows for a final product with less impurities. In the second step, about 1.5 grams of HgO is placed in a quartz tube, along with 2.14 grams of precursor which is placed in an inert zirconium crucible. The reason HgO and the

precursor are kept separate is because it produces crystals with few impurities. Also, the precursor reacts with quartz at high temperatures. In addition, a small amount (~ 40 mg) of $MgSO_4$ is included in the quartz tube for the purpose of producing larger crystals, though this does cause a drop in crystal quality. Once all chemicals are placed in the quartz tube, the tube is sealed with a plug and placed in a furnace.

The synthesis of Hg1201 depends on both temperature and pressure. The reaction itself takes place at about 800°C, but high Hg and O_2 partial pressures are also needed. For this reason, the quartz plug is sealed about 10 cm from the bottom of the tube to provide sufficiently high pressure. As the contents of the tube are heated to about 800°C, the chemicals decompose into the appropriate reaction and Hg1201 is synthesized. At this point, due to the fact that Hg reacts, the pressure decreases rapidly, so it is very important that the pressure is still sufficiently high for the reaction to take place. After this stage, the temperature rises to 1020°C, where the mixture melts to ensure homogeneity. The mixture is then cooled to about 900°C, where crystalline Hg1201 begins to form. Nucleation sites occur near the cooler parts of the mixture. Once this is done, the final product is cooled to room temperature to be removed. In order to pick out crystals from the product, it is put into a humidity box for several days to decompose. Crystals are then picked and prepared for further measurements.

Measurements of as-grown samples

To see if growth results were consistent, certain properties of as-grown crystals were measured. These measurements are done using a Quantum Design Inc. Magnetic Properties Measurement System (MPMS). This system is able to cool samples to critical temperature ranges and is able to measure small changes in magnetic moments using a superconducting quantum interference device (SQUID) magnetometer. The first property measured is the T_c of the sample. This is done simply by measuring the magnetic moment of the sample in an applied magnetic field throughout a wide range of temperatures surrounding its supposed critical temperature. Well above the T_c, the diamagnetic contribution to the moment will be 0, but below the T_c, the magnetic moment becomes very large (due to the Meissner-Ochsenfeld effect and the associated shielding currents) and negative, make the magnetic susceptibility χ equal to -1 (in proper units) Therefore, the temperature at with this drop occurs will be the critical temperature. In practice, there is some width to the T_c, so the T_c is taken to be the temperature at half of the maximum of

the full magnetic moment. The sharper the transition is, the better the sample quality is. For as-grown crystals, critical temperatures are typically around 78 K.

Another measured property is the ratio of the magnetic moments cooled in zero magnetic field (ZFC) and with a magnetic field (FC). This is also known as the FC/ZFC ratio. This is another quantity used to determine the quality of a sample. In a perfect superconductor, the value of the FC/ZFC ratio should be 1, because ideally there should not be any difference between either diamagnetic signals. However, in practice, when a sample is cooled with an applied magnetic field, there will vortices of trapped flux in the direction of the applied magnetic field. These vortices tend to be pinned at impurities within the material, which is a reason the FC/ZFC ratio is a decent measurement of sample quality. The vortices within the material will cancel out part of the diamagnetic signal, which results in a smaller signal overall [6].

The precursor V#1 was prepared in late December of 2013. It was used for eights growths. The as-grown results for one sample grown with precursor V#1, VN6_a, is shown below in Figure 2

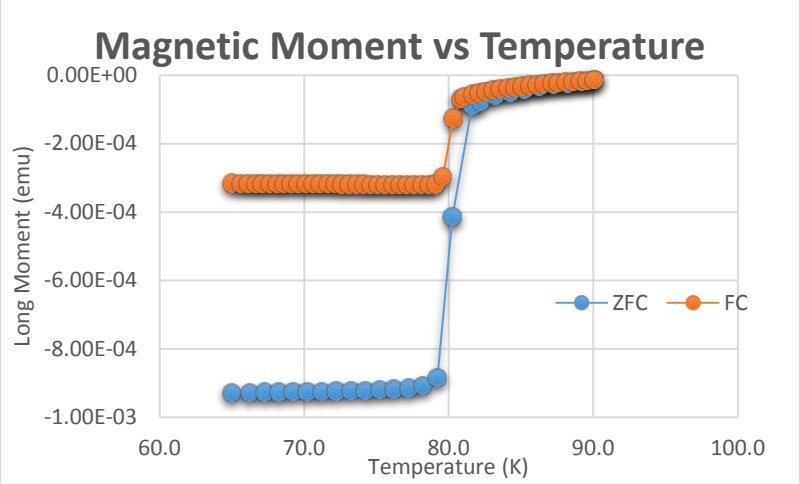

Figure 2: Plot of the magnetic moment vs temperature for the sample VN6_a for both FC (orange) and ZFC (blue) measurements. As expected, the ZFC signal is much greater in magnitude than the FC signal. The signal is negative because the magnetic moment is in the opposite direction of the applied field, since a superconductor is diamagnetic. This sample exhibits a T_c of about 80 K, with a width of about 2 K.

The T_c of this sample is about 80 K, which is typical for as-grown samples. The sample exhibits a fairly sharp transition to the superconducting state, which indicates fairly good crystal quality. The FC/ZFC ratio is about 33%, which is fairly good. Much higher ratios are not extremely common. This sample exhibited the highest ratio of all other samples grown in this project.

It should be noted that there is some slope in the high-temperature part of the curves. Ideally, these parts of the curves should be flat, so that the transition occurs more sharply. The slope indicates that the sample is not uniformly doped. This is because some parts of the sample are transitioning to a superconducting state before others, causing a slight variation in the signal. This non-uniform doping is common in as-grown samples and not really a problem, as the doping should become uniform when crystals are annealed for a period of time.

Annealing Samples

Annealing is the process of adjusting the doping level of a crystal. This is done by placing samples in a tube furnace at some elevated temperature (300+°C) under some pressure condition for a few months at a time. The annealing conditions depend on what doping level is wanted. For a higher doping level, samples are annealed in the presence of O_2 partial pressure. For a lower doping level, samples are annealed in air, nitrogen flow, or a vacuum. Optimally doped (OD) samples have a T_c of about 97 K, while both underdoped (UD) and overdoped (OV) samples have critical temperatures below 97 K. All of these doped samples are desirable to obtain in order to explore the different regimes of the phase diagram.

When looking for good annealed samples, the sharpness of the T_c is the main factor considered. The uniformity of the doping is also considered. The data for an overdoped sample annealed at 300°C with 8 barr of O_2 partial pressure is shown below in Figure 3. It should be noted that this sample is different from the previous as-grown sample.

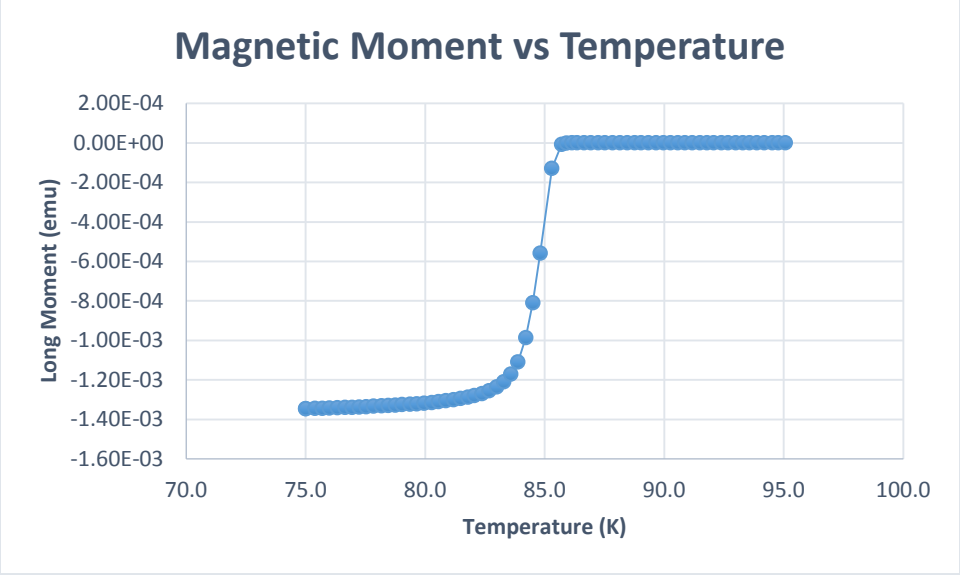

Figure 3: Magnetic moment plot for OV sample. This is a ZFC measurement. Note the very flat portion at the top of the curve. This sample exhibits a T_c of about 84.5 K, with a width of about 2.5 K.

This sample is overdoped because it was annealed with O_2. It is therefore on the right-hand-side of the "T_c dome" located in the phase diagram (Fig. 1). The sample has a T_c of about 84.5 K, which is relatively sharp (with a width of about 2.5 K). Notice that the top part of the curve is much flatter than the previous as-grown plot. This suggests that the doping is much more uniform than in the previous sample. The sample is therefore well-annealed and ready to be used for further measurements.

Conclusion

The data from this study clearly show that the methods used to grow and anneal single crystals of Hg1201 are viable for creating good, high-quality crystals. As-grown samples typically have critical temperatures near 80 K, and the sample presented here in fact had a T_c very nearly on 80 K, with a relatively sharp transition (~2 K). The FC/ZFC ratio of the sample was about 33%, which is difficult to compare to other crystals since it is more variant. It was, however, the highest ratio of all crystals grown with the precursor V#1. The flux method for growing these crystals therefore appears to be very reliable. Annealing conditions proved to be successful as well. With a sample annealed at 300°C and 8 bar, a sharp T_c was observed (~2.5 K), and the oxygen doping appeared to be very homogeneous. This suggests that Hg1201 crystals are less susceptible to disorder due to adding oxygen dopant, since otherwise the sample would be of much lower quality [6].

For future directions of this project, it is important to characterize the different phases in the phase diagram of Hg1201. Therefore, it is necessary to study how thermal, electrical, and magnetic properties change as the different phases are traversed. This can be done by performing transport measurements (thermoelectric power, Hall coefficient, resistivity, etc.) on samples at different doping levels. There is also a desire to reach the more extreme doping levels, which has yet to be done with single crystals of Hg1201.

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